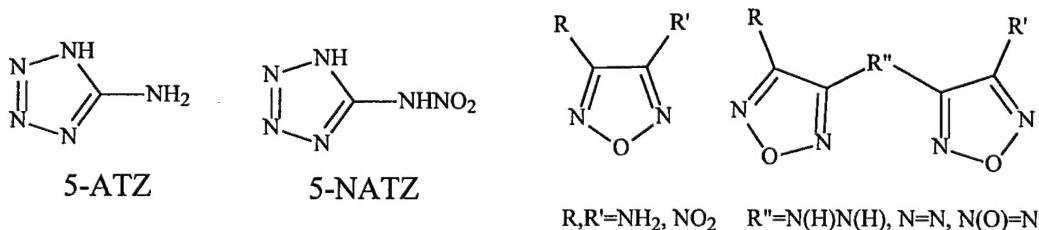


EXECUTIVE SUMMARY

This research program was devoted to the study of high-nitrogen compounds that have been of worldwide interest as gas generators, explosives, and propellants. The focus was specifically on substituted tetrazole and furazan ring compounds. The Russian FLAME database reveals that many of these compounds have high burning rates. In the United States these compounds are of interest to AFRL, Los Alamos National Laboratory, and the Thiokol Corporation as highly energetic materials. The research program required synthesis of most of the compounds, flash pyrolysis studies to identify and quantify the gaseous products, vibrational spectroscopy and X-ray crystallography to determine the structural details, and density functional theory computations. All of this work was aimed at fundamental understanding the energetic behavior of these compounds. The research program has resulted in the awarding of two M.S. degrees in chemistry, the submission of five manuscripts, and presentation of the work at several conferences.

INTRODUCTION

The classes of tetrazole and furazan compounds of interest in this work are the aminotetrazole (5-ATZ) and nitraminotetrazole (5-NATZ) compounds as salts, and the furazan and bifurazan compounds whose structures are shown below. Identification of chemical processes that dominate to determine the burning rate of solid propellant formulations is one of the more prominent motivations of basic research in energetic materials and propellant combustion.¹ The problem is one of extreme complexity because competing variables, such as



changes in the pressure, temperature, formulation, method of analysis, etc., may all affect the supposed role of a given reaction or process. Moreover, the burning rate at one set of conditions may be dominated by gas phase reactions, whereas the condensed phase reactions may dominate at other conditions. Therefore, the chemical process that controls the burning rate and the diagnostic method by which it is identified must be well matched for the particular set of conditions used. Otherwise there is little chance of success.

T-Jump/FTIR spectroscopy creates very fast heating of a film of material to temperatures that typically exist on the surface of the material undergoing steady combustion.²⁻⁴ A relatively constant temperature is maintained in the sample by a very responsive heater circuit, while the gaseous species are identified by rapid scan infrared spectroscopy. By design this device is most sensitive to decomposition processes in the condensed phase and minimizes the processes in the gas phase. This latter condition is accomplished by using a cool inert atmosphere in the cell, which quenches the liberated products and prevents a flame from forming. Consequently, a material whose burning rate is likely to be dominated by condensed phase processes is best

suited for analysis by T-jump/FTIR spectroscopy. The greatest opportunity for success is also likely to rest with materials having relatively few competing pathways of decomposition so that the processes are possibly distinguishable.

Tetrazole derivatives are potentially well suited for determining the controlling mechanism of the burning rate. First, their condensed phase decomposition reactions are frequently exothermic and therefore can be the dominating factors in the rate and temperature of gasification. Second, the possible pathways of tetrazole decomposition are somewhat fewer in number than is the case for most other energetic materials. Third, the burning rates of a number of tetrazole derivatives have been measured by Fogelzang, et al.⁵ In particular, large differences in the burning rates are observed for 5-amino-1H-tetrazole (5-ATZ) and its hydrohalide salts [5-ATZH⁺]X (X = Cl, Br, I). A study of their flash pyrolysis chemistry and resulting products was therefore undertaken. In addition high-nitrogen salts of 5-nitraminotetrazole were synthesized and flash pyrolyzed by T-jump IR and Raman methods developed at the University of Delaware.

Given the great interest shown in the bifurazan compounds, especially by the Russians, a great deal of effort was devoted to studying this category of materials. Some of this work was supported by AFOSR. The synthesis of the compounds required considerable effort. X-ray crystallography was conducted on five of the compounds to determine the crystal and molecular conformations. Ab initio quantum mechanical calculations were performed to calculate the relative heats of formation and the vibrational spectra. Flash pyrolysis of the compounds was determined to identify the gaseous products. A few burning rate data are available from Russian and US sources.

TETRAZOLE-BASED COMPOUNDS

The detail discussion of the chemistry-based origin of burning rate differences of 5-aminotetrazole salts of the hydrogen halides is the subject of a paper in press in Combustion and Flame.⁶ Only a brief summary will be given in this report. The hydrohalide (HCl, HBr, HI) salts of 5-amino-1H-tetrazole (5-ATZ) were flash pyrolyzed under 0.5 MPa of Ar by Temperature-jump/Fourier Transform Infrared Spectroscopy, and the gaseous products were determined at 350°C, 400°C and 450°C. Comparison of the products indicated that two global decomposition pathways exist, which give somewhat different products. The first channel is dissociation of the salt to form HX and 5-ATZ followed by decomposition of neutral 5-ATZ. The second channel involves decomposition of the [5-ATZH]⁺ ion directly. The ratio of these two channels depends on the compound. The first channel is favored over the second channel in the order HCl > HBr > HI, which is the trend of the pK_a values of these acids. This information enables both the ordering of the burning rates as a function of pressure as well as the trend in the pressure dependence of the individual burning rates of these compounds to be rationalized. Figure 1 shows the burning rate data and the IR spectroscopy-determined balance of the two decomposition channels. The study solved the seeming contradiction of why the most mass diluted compound (the I⁻ salt) has highest burning rate.

A second study focused on salts of 5-nitraminotetrazole (5-NATZ) anion with the high nitrogen cations: ammonium, hydrazinium, guanidinium, triaminoguanidinium, and triaminotriazolium.⁷ Some of the compounds have greater than 75% nitrogen by weight. The

gaseous products were characterized by the use of a combination of T-jump/FTIR and T-jump/Raman spectroscopy methods.⁷ No burning rate data are available for these compounds, but they are potentially useful for environmentally safe gas generation.

BIFURAZANS

Figure 2 shows the furazan (1,2,5-oxadiazole) compounds that were the focus of this study. The synthesis of dinitrohydrazofurazan is given for the first time. The molecular structures of five furazan compounds in which two amino- or nitro-substituted furazan rings are bridged by azo, azoxy or hydrazo groups were determined by single crystal X-ray crystallography.⁸ These are diaminoazofurazan, diaminoazoxyfurazan, dinitroazoxyfurazan, diaminohydrazofurazan, and dinitrohydrazofurazan. The structures are compared to those previously reported on dinitroazofurazan, aminonitroazoxyfurazan, and another polymorph of diaminoazoxyfurazan. Figure 3 compares the molecular conformations.

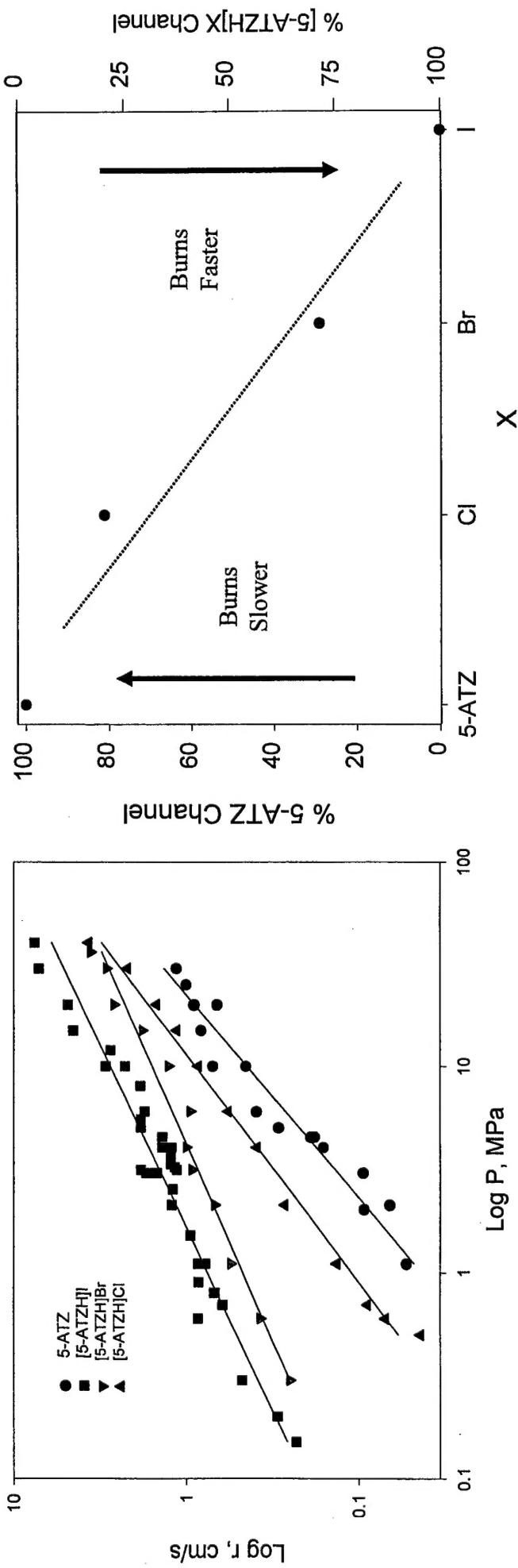
Ab initio density functional theory (DFT) was used to calculate the heats of formation and infrared-active vibrational frequencies of all twelve furazan compounds in Figure 2.⁹ The absolute values of the heats of formation are unreliable but the trends with systematic variations of the bridge and terminal groups are reasonable. The results help rectify the numerous discrepancies in the heats of formation reported by others. The assignments of the vibrational motions to IR frequencies based on a force field analysis are given to clarify the complex coupling in these molecules.

Nine of these energetic furazan compounds were flash-heated by the use of T-jump/FTIR spectroscopy.¹⁰ Thermodynamically relatively stable gaseous products form, which reflect several patterns in the stoichiometry of the parent compound. The hydrazo-bridged furazans lose H₂ to form the azo-bridged analog before the ring decomposes. The melting point and sublimation properties qualitatively relate to the crystal structure and hydrogen bonding potential in these compounds.

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Fig. 1 Burning Rates as a Function of Pressure of
 $\text{[5-ATZH}_2\text{NH}_2\text{]} \text{X}$ ([5-ATZH] H_2) Salts
 and the Percentage of the two Reaction Pathways



As the contribution of the 5-ATZH^+ channel increases, so does the burning rate because the 5-ATZH^+ channel is more exothermic.

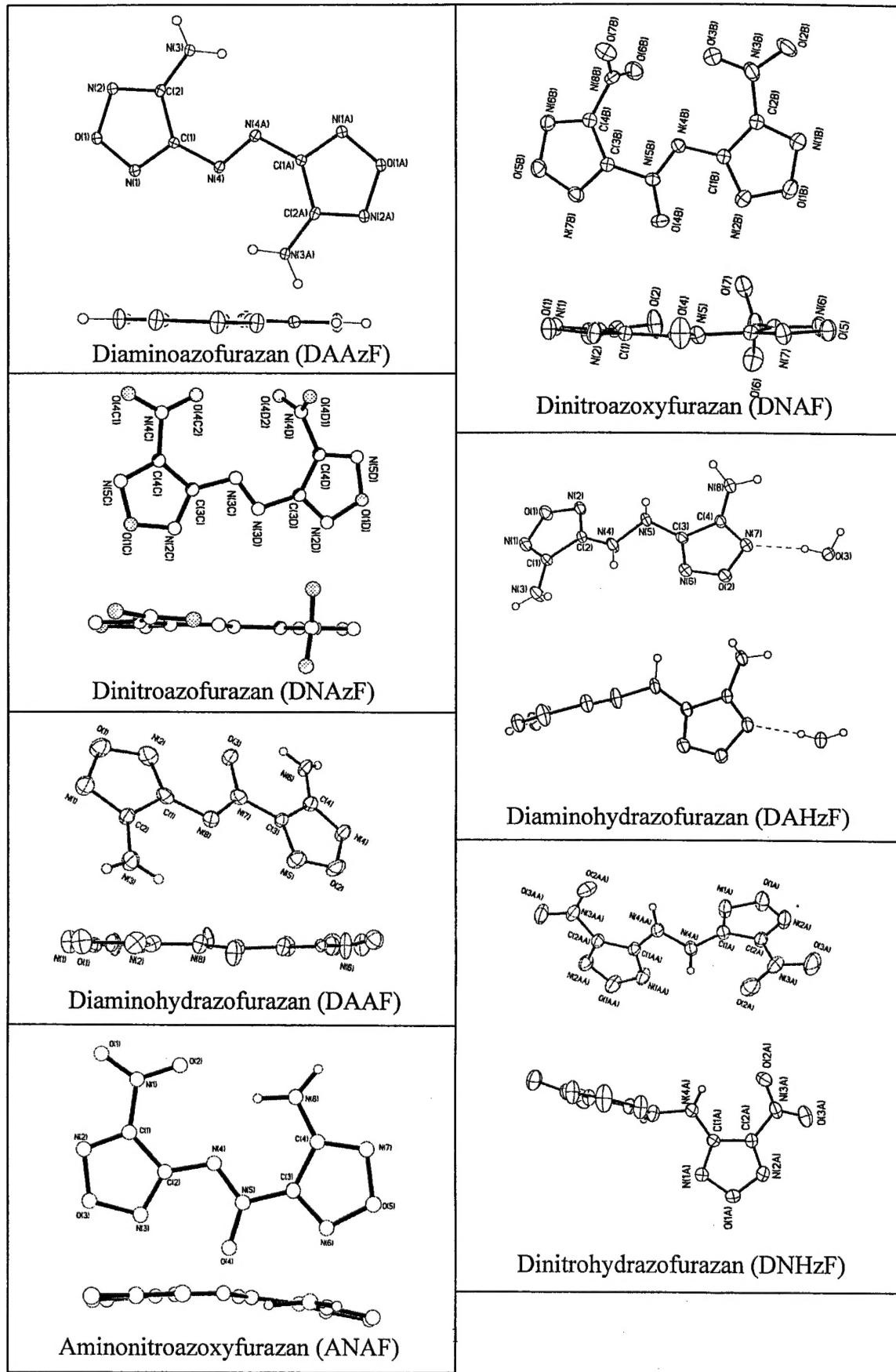
The sensitivity of the burning rate to pressure decreases as the (5-ATZ) channel decreases, e.g. $\text{[5-ATZH]Cl} \longrightarrow \text{HCl} + 5\text{-ATZ}$ (evaporation)

Fig 2. Furazan Flash Pyrolysis Project

Diamino Category Aminonitro Category

Diamino Category		Aminonitro Category		Dinitro Category	
One ring	Diaminofurazan - DAF Gift from Thiokol	C ₂ H ₄ N ₄	Aminonitrofuran - ANF Synthesized	C ₂ H ₂ N ₄ O	Dinitrofuran - DNF Unstable (not considered further) C ₂ N ₄ O ₅
Hydr azo	Diaminohydrazafuran - DAHzF Synthesized	C ₄ H ₆ N ₈ O	Aminonitrohydrazafuran - ANHzF (not considered further)	C ₄ H ₄ N ₈ O	Dinitrohydrazafuran - DNHzF Synthesized
Azo	Diaminoazofuran - DAAzF Synthesized	C ₄ H ₄ N ₈ O	Aminonitroazofuran - ANAzF (not considered further)	C ₄ H ₂ N ₈ O	Dinitroazofuran - DNAzF Synthesized
Azox y	Diaminoazoxyfuran - DAAxF Synthesized	C ₄ H ₄ N ₈ O	Aminonitroazoxyfuran - ANxAF Gift from Air Force	C ₄ H ₂ N ₈ O	Dinitroazoxyfuran - DNAxF Synthesized

Fig. 3 X-ray crystal structures of bifurazan compounds



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